

Laboratory Assessment of Emission Reduction Strategies for the Agricultural Fumigants 1,3-Dichloropropene and Chloropicrin

D. J. ASHWORTH,^{*,†} F. F. ERNST,[†]
R. XUAN,[†] AND S. R. YATES[†]

USDA-ARS, U.S. Salinity Laboratory, 450 W. Big Springs Road, Riverside, California 92507, and Department of Environmental Sciences, University of California, Riverside, California 92521

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With the increased use of the agricultural fumigants 1,3-dichloropropene (1,3-D) and chloropicrin (CP), it is important that strategies to reduce emissions of these fumigant from soil to the air are assessed to protect air quality. Using an established soil column approach, the following emission reduction strategies were compared to a control: (1) spray application of ammonium thiosulfate to the soil surface; (2) deep injection at 46 cm depth; (3) high density polyethylene sealed over the soil surface; (4) virtually impermeable film sealed over the soil surface; and (5) irrigation with ammonium thiosulfate solution. Relative to the control, 1,3-D emissions were reduced by 26.1, 1.0, 0.01, 94.2, and 42.5%, for treatments 1 through 5, respectively. For CP the reductions were 41.6, 23.3, 94.6, 99.9, and 87.5% for treatments 1 through 5, respectively. Virtually impermeable film gave the greatest reductions for both fumigants, while HDPE was very effective only for CP. Despite offering less significant emission reductions, the lower cost alternatives to tarping, particularly irrigation with ATS solution, may offer substantial benefit where tarping is not economically viable.

Introduction

As alternatives to methyl bromide, the agricultural fumigants 1,3-dichloropropene (1,3-D) and chloropicrin (CP) are becoming increasingly popular. In 2006 in California, 3.9×10^6 kg of 1,3-D was used (22.6% of total fumigant use) to treat 1.95×10^4 ha. CP use was 2.3×10^6 kg, treating 2.04×10^4 ha (1). Selected properties of both 1,3-D and CP are given in Table 1. Important characteristics of soil fumigants are their relatively high vapor pressure and Henry's constant, which maintain the chemical in the gaseous phase and facilitate its diffusive transport through the soil pore space. For shank injection to agricultural soils (typically at 30 or 46 cm depth), 1,3-D and CP are commonly applied together as the commercial product Telone C-35 (Dow Agrosciences), which contains 63.4% 1,3-D, 34.7% CP, and 1.9% inert ingredients. In California, the product Telone C-35 CA is used and contains 61.1% 1,3-D, 34.7% CP, and 4.2% inert

ingredients. These fumigant chemicals have recently received much attention to assess their potential for transfer from soil to air. Soil-to-air transfer is an environmental concern due to the potential for direct human exposure of the chemicals to those near the application site (e.g., agricultural workers and local populations) and the potential for the fumigant to serve as the volatile organic compound (VOC) component in the formation of photochemical smog (near-surface ozone). The label for Telone C-35 specifies the requirements of adequate soil moisture above the point of injection and a buffer zone of at least 30.5 m from any occupied structure (this distance is increased to 91.4 m in California). Such measures serve to limit the extent and impact of soil-to-air emissions. However, designing and assessing strategies to dramatically reduce emissions of agricultural fumigants is a critical research need to ensure agricultural productivity in the face of increasingly stringent air quality regulation.

As an emission reduction strategy, plastic tarps covering the soil surface postfumigation serve to physically limit the transfer of fumigant across the soil-air boundary. These tarps are typically classified, in order of decreasing permeability, as follows: low density polyethylene (LDPE); high density polyethylene (HDPE); semi-impermeable film (SIF); and virtually impermeable film (VIF). Several workers have demonstrated the ability of HDPE and, particularly, VIF to reduce the emissions of either 1,3-D or CP from agricultural soils (2–4). However, the different tarps vary in their permeability to fumigants. Moreover, a single tarp can have differing permeability characteristics for different fumigants. Consequently, although the order of decreasing tarp permeability given above is useful as an indicator of a tarp's emission reduction potential, it does not necessarily hold across all tarp/fumigant combinations. Therefore, selecting a tarp based solely on this nomenclature may not necessarily produce the desired effect in terms of emission reduction. It is therefore preferable for the mass transfer coefficients (*h* values) of tarps to also be reported, based on their permeability to a range of fumigants (5). This allows for a more objective selection of a tarp for a given scenario. It also allows for a more meaningful comparison of tarp effectiveness (e.g., across different studies).

The application of ammonium thiosulfate (ATS) to the soil surface prior to fumigation has the potential to reduce fumigant emissions by stimulating the thiosulfate-induced dehalogenation of the fumigants via nucleophilic substitution (6–8). Significant reductions in the half-life of both 1,3-D and CP have been observed due to the presence of ATS (9, 10). A consequential reduction in emissions of these fumigants has thus also been observed when ATS was applied (7, 11). Due to the increased path length between the point of injection and the soil surface, deep injection potentially reduces and delays fumigant emissions. Additionally, the increased contact time between the fumigant and degradative soil surfaces (e.g., organic materials) further serves to reduce emissions under this management strategy. There is a paucity of information relating to the effect of deep injection on the emissions of 1,3-D and CP from agricultural soils. However, for MeBr, it was estimated that emissions could be reduced from 87% to 60% when injection depth is increased from 25 to 60 cm (12). Moreover, Yates et al. (13) found that MeBr emissions were reduced from 65% to 21% due to deep injection. Similarly, in laboratory soil columns, MeBr emissions were reduced by 54% in nontarped soils when injection depth was increased from 20 to 60 cm. In laboratory studies, a 40% reduction was found for tarped conditions (14).

* Corresponding author e-mail: daniel.ashworth@ars.usda.gov.

[†] USDA-ARS.

[†] University of California.

TABLE 1. Selected Properties of 1,3-D and CP^a

property	1,3-dichloropropene ^b	chloropicrin
formula	C ₃ H ₄ Cl ₂	CCl ₃ NO ₂
vapor pressure (kPa)	4.6 (<i>cis</i>), 3.1 (<i>trans</i>) @ 25 °C	2.4 @ 20 °C
boiling point (°C)	104 (<i>cis</i>), 113 (<i>trans</i>)	112
density (g mL ⁻¹)	1.22 @ 20 °C	1.65 @ 20 °C
solubility (g L ⁻¹)	2.3 (<i>cis</i>), 2.2 (<i>trans</i>) @ 25 °C	1.6 @ 20 °C
Henry's constant (K _H)	0.056	0.093
HDPE h-value (cm h ⁻¹) ^c	2.0 (<i>cis</i>), 3.7 (<i>trans</i>) @ 20 °C	0.6
VIF h-value (cm h ⁻¹) ^c	0.001 (<i>cis</i>), 0.002 (<i>trans</i>) @ 20 °C	0.0002

^a All data except tarp h-values are taken from refs 28 and 29. ^b 1,3-D has two isomers, *cis* and *trans*. ^c Tarp h-values determined in preliminary experiments according to the procedure of Papiernik et al. (5) for the HDPE and VIF used in this study.

The effects of water sealing and soil organic matter content on emissions of *cis* 1,3-D from a soil collected from Buttonwillow, CA have been previously studied in the laboratory (15) and demonstrated a two times reduction in emissions due to irrigation and a five times reduction due to organic matter enrichment. Under field conditions, irrigation of the same (Buttonwillow) soil led to emissions of 10–15% of applied 1,3-D (16). These authors suggested that this level of emissions represented a 30–50% reduction of the total emission losses compared to conventional fumigant applications in field and field plot studies. Using the Buttonwillow soil, the primary aim of the present work was to continue the assessment of fumigant emission reduction strategies by determining the total emission losses for a number of further treatments. The effects of HDPE tarp, VIF tarp, ATS application, and deep injection on the soil surface emissions of 1,3-D and CP from agricultural soil are quantified. Rarely have such a wide variety of strategies been assessed in a single soil type, meaning that rigorous comparisons of all these treatments have not previously been made.

Materials and Methods

Reagents and Soil. Stock solutions of Telone II (98.9% purity; 50:50 *cis* 1,3-D: *trans* 1,3-D ratio) and chloropicrin (99.9% purity) were donated by Dow Agrosiences (Indianapolis, IN). Ammonium thiosulfate was obtained from Sigma Aldrich (Milwaukee, WI), hexane (GC-MS/HPLC grade) and acetone (HPLC grade) from Fisher Scientific (Fairlawn, NJ), and XAD-4 (2 section 400/200 mg) and Anasorb CSC charcoal (2 section 400/200 mg) sorbent tubes from SKC Inc. (Eighty Four, PA). Deionized water was used for making up solutions. Sandy loam soil (60% sand, 30% silt, 10% clay) was collected from farmland near Buttonwillow, CA (thermic Typic Haplargids; Milham series). The soil was collected in depth increments of 0–15, 15–30, 30–45, 45–60, and >60 cm into clean plastic buckets and sealed to prevent moisture loss. Fumigant degradation rates in this soil were determined in preliminary experiments using the method described by Ashworth and Yates (15). At 25 °C, half-lives were measured as 90 and 2.9 h for 1,3-D and CP, respectively. A 1 mil, clear HDPE tarp was supplied by Dow Chemical Company (Midland, MI), and a 1.5 mil, clear VIF (Hytibar) was supplied by Klerk's Plastics (Hoogstraten, Belgium). Mass transfer coefficients (h values) of the tarps were determined in preliminary experiments using the approach previously described (5). These values indicate the much lower permeability of the VIF to fumigant vapors and the low permeability of both tarps to CP compared to 1,3-D (Table 1).

Soil Column Experiments. The general nature of the soil column design has been described previously (14). Soil was packed into cylindrical (12 × 150 cm) stainless steel columns as per the field depth increments. Field-measured bulk density and moisture content of the soil was maintained in

the columns. A dry bulk density of 1.5 g cm⁻³ was used throughout the soil column (determined throughout the field profile as 1.5 (±0.09) g cm⁻³). Volumetric moisture contents were as follows: 0–15 cm, 13%; 15–30 cm, 17%; 30–45, 45–60, and >60 cm, 19%. A stainless steel emissions chamber placed on the surface of the soil column was swept with clean air at a rate of 80 mL min⁻¹ to channel emitted fumigant through first a XAD-4 and then a charcoal sorbent tube (tubes connected in series). In previous studies, a flow rate of 150 mL min⁻¹ has been used for these columns (15). However, a relatively low flow rate was used here because it has been recently noted that breakthrough of chloropicrin from XAD-4 tubes can occur at high flow rates (17). It was not expected that using the 80 mL min⁻¹ flow rate would have any impact on gas diffusion into the headspace. Liquid fumigants were injected into the soil column using a glass syringe fitted with a side-port needle. Injection was carried out at 11:00 h on day 0. For Telone II, 150 µL were injected and for CP, 60 µL. This equates to application rates of approximately 161 and 88 kg ha⁻¹, respectively. The ratio of Telone II to CP was chosen to approximate that of the commercial product Telone C-35. Near-surface soil temperatures were manipulated by programming the ambient temperature of the room in which the column experiments were conducted. A diurnal temperature regime that resulted in soil temperatures typical of those observed at the field site in September 2007 was employed. This gave temperatures ranging from 23 to 32 °C at 5 cm soil depth in the soil columns. Below 30 cm depth, the columns were insulated with 1 cm thick foam to reduce temperature fluctuations at depth.

A number of emission reduction strategies were assessed and compared to a control (no emission reduction strategy) treatment, *viz*: deep injection, ATS sprayed onto the soil surface (ATS_{spray}), HDPE sealed over the soil surface, VIF sealed over the soil surface, and ATS applied with irrigation water to the soil surface (ATS_{irrigation}). In all but one case, fumigants were applied at 30 cm depth. The exception was the deep injection treatment where a depth of 46 cm was used. In the ATS_{spray} treatment, approximately 565 mg of ATS in approximately 1.6 mL of water was sprayed to cover the soil surface directly prior to fumigation. In the ATS_{irrigation} treatment, the same amount of ATS was added but in 113 mL (1 cm depth) of water. These treatments equate to an application of 50 g m⁻² and a thiosulfate:Telone C-35 ratio of 1:1.7. The HDPE and VIF tarps were applied over the soil surface and sealed between the soil column and the emissions chamber using epoxy resin so as to produce a leak-free covering. Except for the ATS_{irrigation}, each treatment was duplicated. Most treatments were run for 14 days, except for the tarped treatments which, at 15 days, had the tarps ripped using a hooked device temporarily inserted into the emissions chamber. This was done to simulate and assess the effect of tarp removal, or tarp ripping for planting purposes, on fumigant emissions over the following 2 days.

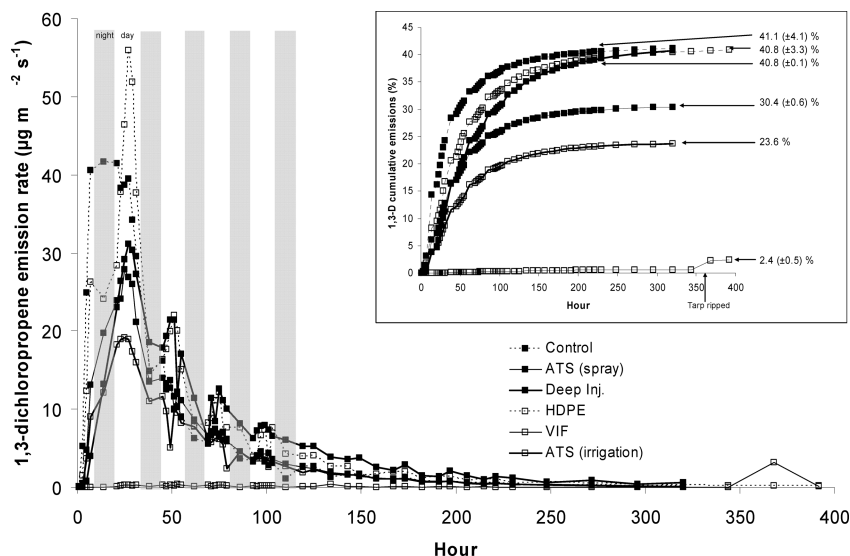


FIGURE 1. 1,3-D emission rates and cumulative emissions (inset) for each treatment.

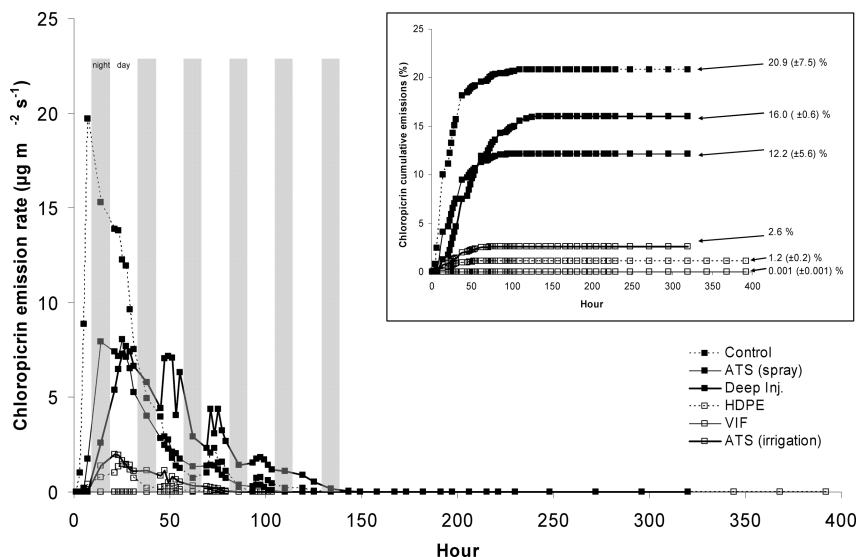


FIGURE 2. Chloropicrin emission rates and cumulative emissions (inset) for each treatment.

Initially, a sampling period of 2 h was used for each pair of sorbent tubes (XAD-4 and charcoal) between 07:00 and 19:00 h and a period of 12 h between 19:00 and 07:00 h (i.e., a single tube was used overnight). The 2-h period was extended later in the experiment when the rate of fumigant release from the soil was expected to be slower. Sampled tubes were stored at -19°C until extraction and analysis. XAD-4 tubes were extracted first by separating their two sections and placing each into 20 mL glass vial. After the addition of 4 mL hexane, the vials were immediately capped with a Teflon-faced butyl rubber septum and an aluminum crimp seal and shaken for 30 min, and around 1.5 mL of the supernatant solution was transferred to a glass vial for analysis. In some cases significant breakthrough of the fumigants onto the 'B' section of the XAD-4 tubes was observed. In these cases, the charcoal 'backup' tubes were also extracted and analyzed. This procedure demonstrated that no fumigant broke through the XAD-4 onto the charcoal tubes. The charcoal tubes were extracted in the same way as the XAD-4 but using acetone in place of hexane.

Analysis of XAD-4 and charcoal tubes was carried out using an Agilent Technologies 7890C gas chromatograph (GC), equipped with a microelectron capture detector. The column was a DB-VRX 122-1534 with dimensions of $30\text{ m} \times 250\text{ }\mu\text{M} \times 1.4\text{ }\mu\text{m}$ (Agilent Technologies) running at a flow

rate of 1.6 mL min^{-1} and with He as the carrier gas. The inlet temperature was 240°C , and the detector temperature was 290°C . The GC oven temperature was maintained at 45°C for 1 min after sample injection, increasing to 75°C at a rate of $2.5^{\circ}\text{C min}^{-1}$, and then increasing to 140°C at a rate of $35^{\circ}\text{C min}^{-1}$ before being held at this temperature for 3 min. Under these conditions, retention times of *cis* 1,3-D, *trans* 1,3-D, and CP were 10.4, 11.7, and 13.1 min, respectively. A set of ten standards encompassing the range of concentrations of the samples was prepared in the same solvent as the samples. For all analyses, concentrations of total 1,3-D were calculated from the *cis* and *trans* data, and they are the total values reported here.

Results and Discussion

Fumigant Emission Rates. The emission rates of the fumigants from the soil surface are shown in Figures 1 and 2 for 1,3-D and CP, respectively. This information is an important measure in assessing the risk associated with fumigant use in the field since it controls air concentrations and hence exposure to agricultural workers and nearby populations. Overall, the lower emission rates observed for CP were expected due to the lower application rate (approximately half that of 1,3-D), its shorter half-life, and its lower vapor pressure (Table 1). In the majority of treatments,

emissions of CP occurred over a period of around 100 h (to around 125 h in the deep injection treatment). In contrast, the emission rate curve for 1,3-D showed extensive tailing beyond this period. This difference was most likely the result of the much shorter degradation half-life determined for CP compared to 1,3-D. In the control columns, the peak emission rate was reached more rapidly (after 7 and 14 h for the CP and 1,3-D, respectively) than for any of the treatments. Rates at these times were approximately 20 and 42 $\mu\text{g m}^{-2} \text{s}^{-1}$, respectively. In field experiments (18), it was noted that earliest and highest emissions of 1,3-D and CP occurred in control soils, with the maximum rate observed 15 h after fumigation. It has also been suggested (19) that maximum 1,3-D emission rate from field control soil occurred during the first night following application. In 63.5×15.5 cm columns (11), the maximum emission rate of cis 1,3-D was reported 15 h after fumigation. For CP, maximum emission rate took place 11 h after fumigation (2). These results are in very good agreement with those of the present experiment and indicate that in the absence of an emission reduction strategy, fumigant emissions are likely to be the greatest during the first evening and night-time period after application.

The maximum emission rate for each treatment generally occurred 1 day after fumigation, indicating that each emission reduction strategy delayed the release of fumigants relative to the control. At this time, the decreasing order of the emission rate maxima was as follows: HDPE > Control > Deep Injection > ATSSpray > ATSIrrigation > VIF for 1,3-D and Control > ATSSpray > Deep Injection > ATSIrrigation > HDPE > VIF for CP. Therefore, except for 1,3-D in the HDPE treatment, the emission reduction strategies reduced emission rates relative to the control. VIF was most effective at reducing emission rates due to its low h-values (Table 1). Up to the time that the tarps were ripped, the maximum emission rates from the VIF treatment were just 0.37 $\mu\text{g m}^{-2} \text{s}^{-1}$ for 1,3-D and 0.001 $\mu\text{g m}^{-2} \text{s}^{-1}$ for CP (around 0.9 and 0.005% of the maximum rates for the control, respectively), and these values further reflect the lower h-value determined for CP (Table 1). Upon ripping of the VIF, a spike of 1,3-D (3.2 $\mu\text{g m}^{-2} \text{s}^{-1}$) was observed, indicating that the fumigant was maintained in the soil up to this time. While this is probably beneficial in terms of maintaining pesticidal efficacy within the soil, it also presents an increased risk of exposure to agricultural workers during tarp removal/ripping for planting operations. No other tarp/fumigant combination produced this spike. Of the nontarped treatments, deep injection and both ATS treatments were effective in reducing emission rates compared to the control. Most marked reductions were observed for the ATSIrrigation treatment, particularly for CP. The effect of deep injection on the time-course trend in CP emissions is also worth noting. Despite markedly reducing the magnitude of the emission rates (relative to the control) up to the end of day 1, the deep injection then led to a continued release of CP, characterized by relatively high emission rates over several days. Although not as pronounced relative to the other treatments, a similar trend was observed for 1,3-D. Based on the observations of the soil gas distribution (not presented here), it is thought that the propensity of the fumigants in the deep injection treatment to diffuse downward to a greater extent than the other treatments is likely to explain the subsequent slow release from the soil surface.

Figures 1 and 2 show emission rates in relation to the 'daytime' and 'nighttime' temperature regime. Under field conditions, differences in both wind speed and temperature are likely to be the primary factors causing differences in daytime and nighttime fumigant emissions. Although temperature was manipulated in our experiments, the effect of wind speed on emissions was assumed to be constant. From day 1 onward, each treatment showed peaks in fumigant

emissions during the daytime periods. These were likely associated with the higher temperatures during these periods, particularly between 12:00 and 18:00 h when soil temperature at 5 cm depth increased from 25 to 32 °C. Since fumigant vapor pressure increases with increasing temperature, higher emissions would be expected during this time when compared to the cooler nighttime periods. Such an effect was observed in similar soil columns with diurnally fluctuating temperatures for 1,3-D (15). Additionally, tarped soils can exhibit greater fumigant emission rates under conditions of higher temperature due to an increase in tarp permeability (20, 21).

Cumulative Fumigant Emissions. The cumulative fumigant emissions, expressed as a percentage of the total amount added, over the course of the experiment are shown in Figures 1 and 2 (insets) for 1,3-D and CP, respectively. In each case, the emission curves reach a plateau indicating that emission from the soil was complete. It is assumed that the remaining fraction of fumigant was degraded within the soil, although it is also possible that small amounts became adsorbed onto soil surfaces such as organic matter (22–24). The plateaus were reached more rapidly for the CP (generally within ~100 h) than for 1,3-D (generally within ~250 h), probably as a result of the more rapid degradation of the CP within the soil. For both fumigants, it is noticeable that the control columns exhibited a more rapid rate of emissions over the early part of the experiment (steeper cumulative emissions curve), indicating that each of the various treatments had an effect on the dynamics of fumigant release from the soil irrespective of whether they reduced total emissions. However, the total loss of fumigant is the most useful means of assessing the effectiveness of emission reduction strategies. In this regard, the HDPE and deep injection offered no benefit in terms of 1,3-D emission reduction when compared to the control (all yielding around 41% total emissions). In the case of HDPE, this has been previously noted by other workers (3, 18, 19) and is consistent with the relatively high 1,3-D permeability values determined for this tarp—an average of 2.85 cm h^{-1} for cis/trans 1,3-D (Table 1). Compared to the value of 0.6 cm h^{-1} for CP, it is not surprising that emissions of CP were reduced (in contrast to 1,3-D) in the HDPE treatment (1.2%) when compared to the control (20.9%). Moreover, the h-values for the tarps were determined under more controlled conditions than those present in the columns. In the columns for example, changes in temperature and humidity at the soil-tarp interface as well as the presence of more than one fumigant may have affected tarp permeability. Deep injection emissions of CP (16.0%) were also reduced from control levels. The reason for this difference in the behavior of the two fumigants in the HDPE and deep injection treatments may be the lower vapor pressure of the CP which would likely limit its ability to diffuse as effectively from the deeper soil or through the HDPE tarp, thus leading to lower emissions. The effectiveness of HDPE in reducing emissions of CP has been reported (2, 19), as has the potential for fumigant emission reduction by deep injection (13, 25).

Most marked emission reductions for both fumigants were obtained by using the VIF tarp which produced total emissions of just 0.001% for CP, representing a $\sim 2 \times 10^4$ times reduction from the control levels. Emission reductions of 1,3-D from the VIF tarped treatment were more moderate and were also significantly affected by the ripping of the tarp toward the end of the experiment. Immediately before ripping, total emissions were just 0.6% but increased to 2.4% afterward. In contrast, an increase in CP emissions was not observed following tarp ripping, probably due to its degradation within the soil by this time. For the same reason, ripping of the HDPE tarp did not result in an increase in CP emissions. The absence of an emissions increase for 1,3-D

spike following ripping of the HDPE tarp was presumably due to the ineffectiveness of the HDPE in maintaining 1,3-D within the soil during the earlier part of the experiment. Several other workers have reported 1,3-D and CP emission reductions when tarps are used. For example, emissions of CP shank injected (30 cm) into soil columns (similar to those used here) were reduced from 82% in the control to 20% by HDPE and to 4% by VIF (Hytibar) film (2). Also in column experiments with HDPE cover (26), emissions of 30% for shank injected (at 20 cm) CP were recorded. Under field conditions (27), CP emissions of 9.5 and 18% were found for two different soils with 20–25 cm shank injection and HDPE cover. Again under field conditions (19), emissions of 9.2% for HDPE and 1.2% for VIF have been reported for CP shank injected at 46 cm. Moreover, CP emissions were reduced from 30% to 17% and 8% for HDPE and VIF, respectively, under similar conditions (18). For 1,3-D, soil column studies (11) have demonstrated that with a 30 cm shank injection, emissions can be reduced from 50.6% to 23.9% using HDPE with a soil surface application of ATS and to 16.2% using HDPE with a soil surface application of manure (application of 'ATS only', and 'manure only' gave emissions of 39.5 and 28.8%, respectively). Also for a 30 cm shank injection to soil columns (3), emissions of 1,3-D were found to be reduced from 50.6% to 44.9% using HDPE and to 9.9% using VIF. Clearly, therefore, HDPE does under some circumstances lead to a reduction in 1,3-D emissions. However, intercomparisons are difficult based only on tarp nomenclature such as 'HDPE' which is essentially an arbitrary designation. It is quite possible that the various HDPE tarps used in such studies had markedly differing h-values, and that may account for differences in emission reduction potential.

Like previous work, the addition of ATS to the surface of the soils in the current work reduced fumigant emissions. In the case of 1,3-D, total emissions were reduced from 41% in the control to 30% in the ATS_{spray} treatment and 24% in the ATS_{irrigation} treatment. In similar experiments (7), it was found that for a 30 cm shank injection to soil columns, emissions of *cis* 1,3-D were reduced from 47.5% in the control to 14.5, 6.4, and 3.4% when ATS was applied at rates of 64, 129, and 193 g m⁻² in 9 mm water, respectively. In recent studies (11), it was reported that for a 30 cm shank injection of *cis* 1,3-D to soil columns, the 50.6% emissions from the control could be reduced to 43.4% and 39.5% when ATS was applied at a 1:1 ATS:fumigant or a 2:1 ATS:fumigant ratio, respectively. Similarly, in drip applied field plots *cis* 1,3-D emissions were reduced from 32.2% to 12.9% when ATS was applied at 32 g m⁻² (7). Despite the same amount of ATS being applied in both ATS treatments in the present experiment, the greater volume of solution in the irrigated treatment apparently induced the better emission reductions, presumably due to a better distribution of the ATS throughout the upper soil layer. Thus, the likelihood of chemical interaction between the ATS and the upward-diffusing fumigants was increased. The influence of the volume of ATS solution on (*cis*) 1,3-D emissions has also been previously studied (7). For an ATS addition of 64 g m⁻², it was found that compared to 43.1% emissions for the control, ATS application in 1, 3, and 9 mm of water gave emissions of 33.4, 23.1 and 12.4%. In addition to an enhanced chemical effect, the greater volume of water is also likely to reduce emissions by physically restricting gas diffusion through the soil pore space (3, 11, 15, 18).

Table 2 shows the emission reduction potential of each of the treatments we have assessed for this soil, i.e. the present data, and that from our previous study (15). Tarping is often the favored approach for reliably reducing fumigant emissions. Clearly, the VIF tarp is a very effective strategy for reducing emissions of the fumigants, which in turn is also likely to maximize the efficacy of these pesticides within the

TABLE 2. Reduction in Emission Loss from Soil Relative to Control (Expressed As a Percentage)

treatment	1,3-dichloropropene	chloropicrin
ATS _{spray}	26.1	41.6
deep injection	1.0	23.3
HDPE	0.01	94.6
VIF	94.2	99.9
ATS _{irrigation}	42.5	87.5
irrigation ^{a,b}	48.3	n.d. ^d
organic matter enrichment ^{a,c}	82.8	n.d. ^d

^a Data from a previous study using the same soil (15) for *cis* 1,3-D. ^b Columns were irrigated with 1 cm of water per day for the first 5 days. ^c Soil organic matter increased from 2.1 to 3.2% by the addition of green waste. ^d n.d.: not determined.

soil. If these were the only considerations, the use of VIF (or, more specifically, tarps with very low h values) should be recommended for widespread agricultural use. However, this is tempered by the economic disadvantages of tarp use. The cost of using HDPE in California has been estimated as around \$2200 ha⁻¹ (\$1300 ha⁻¹ for tarp and glue; \$650 ha⁻¹ for application and \$250 ha⁻¹ for removal and disposal) (18), and use of VIF is likely to exceed this (19) due to the greater level of technology involved in producing this tarp. Clearly, HDPE tarp can produce substantial emission reductions for CP (95%) and could therefore be considered a cheaper alternative to VIF for this situation. Moreover, ATS treatment, particularly when applied as an irrigation, also gave marked (albeit less so than the tarps) reductions for CP. However, the apparent requirement for VIF in order to produce dramatic (94%) 1,3-D emission reductions presents a significant challenge to regulators and farmers. Nevertheless, this work has shown that despite the effectiveness of HDPE (for CP) and VIF, other strategies may offer substantial emission reduction benefits. Irrigation, either with or without ATS, apparently has the potential to reduce 1,3-D emissions by 40–50%. Even more substantial is the 83% reduction in 1,3-D emissions observed for organic matter addition. This level of reduction is close to that observed for 1,3-D in the VIF treatment and suggests that organic matter enrichment of soils may represent an effective, low cost approach to reducing fumigant emissions.

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Literature Cited

- (1) California Department of Pesticide Regulations. *Summary of Pesticide Use Report Data 2006 Indexed by Chemical*; Sacramento, CA, 2007.
- (2) Gan, J.; Yates, S. R.; Ernst, F. F.; Jury, W. A. Degradation and volatilization of the fumigant chloropicrin after soil treatment. *J. Environ. Qual.* **2000a**, *29*, 1391–1397.
- (3) Gao, S.; Trout, T. J. Using surface water application to reduce 1,3-dichloropropene emission from soil fumigation. *J. Environ. Qual.* **2006**, *35*, 1040–1048.
- (4) Gao, S.; Trout, T. J.; Schneider, S. Evaluation of fumigation and surface seal methods on fumigant emissions in an orchard replant field. *J. Environ. Qual.* **2008**, *37*, 369–377.

- (5) Papiernik, S. K.; Yates, S. R.; Gan, J. An approach for estimating the permeability of agricultural films. *Environ. Sci. Technol.* **2001**, *35*, 1240–1246.
- (6) Gan, J.; Yates, S. R.; Becker, J. O.; Wand, D. Surface amendment of fertilizer ammonium thiosulfate to reduce methyl bromide emissions from soil. *Environ. Sci. Technol.* **1998**, *32*, 2438–2441.
- (7) Gan, J.; Becker, J. O.; Ernst, F. F.; Hutchison, C.; Knuteson, J. A.; Yates, S. R. Surface application of ammonium thiosulfate fertilizer to reduce volatilization of 1,3-dichloropropene from soil. *Pest Manage. Sci.* **2000b**, *56*, 264–270.
- (8) Wang, Q.; Gan, J.; Papiernik, S. K.; Yates, S. R. Transformation and detoxification of halogenated fumigants by ammonium thiosulfate. *Environ. Sci. Technol.* **2000**, *34*, 3717–3721.
- (9) Zheng, W.; Papiernik, S. K.; Guo, M.; Yates, S. R. Competitive degradation between the fumigants chloropicrin and 1,3-dichloropropene in unamended and amended soils. *J. Environ. Qual.* **2003**, *32*, 1735–1742.
- (10) Qin, R.; Gao, S.; McDonald, J. A.; Ajwa, H.; Shem-Tov, S.; Sullivan, D. A. Effect of drip application of ammonium thiosulfate on fumigant degradation in soil columns. *J. Agric. Food Chem.* **2007**, *55*, 8193–8199.
- (11) McDonald, J. A.; Gao, S.; Qin, R.; Trout, T. J.; Hanson, B. D. Thiosulfate and manure amendment with water application and tarp on 1,3-dichloropropene emission reductions. *Environ. Sci. Technol.* **2008**, *42*, 398–402.
- (12) Wang, D.; Yates, S. R.; Ernst, F. F.; Gan, J.; Gao, F.; Becker, J. O. Methyl bromide emission reduction with field management practices. *Environ. Sci. Technol.* **1997**, *31*, 3017–3022.
- (13) Yates, S. R.; Wang, D.; Ernst, F. F.; Gan, J. Methyl bromide emissions from agricultural fields: bare-soil, deep injection. *Environ. Sci. Technol.* **1997**, *31*, 1136–1143.
- (14) Gan, J.; Yates, S. R.; Spencer, W. F.; Yates, M. V.; Jury, W. A. Laboratory scale measurements and simulations of effect of application methods on soil methyl bromide emission. *J. Environ. Qual.* **1997**, *26*, 310–317.
- (15) Ashworth, D. J.; Yates, S. R. Surface irrigation reduces the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* **2007**, *41*, 2231–2236.
- (16) Yates, S. R.; Knuteson, J.; Ernst, F. F.; Zheng, W.; Wang, Q. Effect of sequential surface irrigations on field-scale emissions of 1,3-dichloropropene. *Environ. Sci. Technol.* **2008**, *42*, 8753–8758.
- (17) Ashworth, D. J.; Zheng, W.; Yates, S. R. Determining the breakthrough of the soil fumigant chloropicrin from 120 mg XAD-4 sorbent tubes. *Atmos. Environ.* **2008**, *42*, 5483–5488.
- (18) Gao, S.; Trout, T. J.; Schneider, S. Evaluation of fumigation and surface seal methods on fumigant emissions in an orchard replant field. *J. Environ. Qual.* **2008**, *37*, 369–377.
- (19) Gao, S.; Trout, T. J. Surface seals reduce 1,3-dichloropropene and chloropicrin emissions in field tests. *J. Environ. Qual.* **2007**, *36*, 110–119.
- (20) Wang, D.; Yates, S. R.; Gan, J.; Knuteson, J. A. Atmospheric volatilization of methyl bromide, 1,3-dichloropropene, and propargyl bromide through two plastic films: transfer coefficient and temperature effect. *Atmos. Environ.* **1999**, *33*, 401–407.
- (21) Papiernik, S. K.; Yates, S. R. Effect of environmental conditions on the permeability of high density polyethylene to fumigant vapors. *Environ. Sci. Technol.* **2002**, *36*, 1833–1838.
- (22) Kim, J. H.; Gan, J.; Farmer, W. J.; Yates, S. R.; Papiernik, S. K.; Dungan, R. S. Organic matter effects on phase partition of 1,3-dichloropropene in soil. *J. Agric. Food. Chem.* **2003**, *51*, 165–169.
- (23) Xu, J. M.; Gan, J. Y.; Papiernik, S. K.; Becker, J. O.; Yates, S. R. Incorporation of fumigants into soil organic matter. *Environ. Sci. Technol.* **2003**, *37*, 1288–1291.
- (24) Park, M. K.; Kim, J. H.; Dungan, R. S. Sorption of the fumigant 1,3-dichloropropene on soil. *J. Environ. Sci. Health, Part B* **2004**, *B39*, 603–612.
- (25) Papiernik, S. K.; Dungan, R. S.; Zheng, W.; Guo, M.; Lesch, S. M.; Yates, S. R. Effect of application variables on emissions and distribution of fumigants applied via subsurface drip irrigation. *Environ. Sci. Technol.* **2004**, *38*, 5489–5496.
- (26) Zhang, Y.; Wang, D. Emission, distribution and leaching of methyl isothiocyanate and chloropicrin under different surface containments. *Chemosphere* **2007**, *68*, 445–454.
- (27) Wang, D.; Juzwik, J.; Fraedrich, S. W.; Spokas, K.; Zhang, Y.; Koskiken, W. C. Atmospheric emissions of methyl isothiocyanate and chloropicrin following soil fumigation and surface containment treatment in bare-root forest nurseries. *Can. J. For. Res.* **2005**, *35*, 1202–1212.
- (28) Ajwa, H. A.; Trout, T.; Mueller, J.; Wilhelm, S.; Nelson, S. D.; Soppe, R.; Shatley, D. Application of alternative fumigants through drip irrigation systems. *Phytopathology* **2002**, *92*, 1349–1355.
- (29) Van Wesenbeeck, I. J.; Knuteson, J. A.; Barnekow, D. E.; Phillips, A. M. Measuring flux of soil fumigants using the aerodynamic and dynamic flux chamber methods. *J. Environ. Qual.* **2007**, *36*, 613–620.

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